MRL-TR-89-32

AR-005-734

METHODS FOR IMPROVING THE FLOWABILITY OF A PERCUSSION PRIMER COMPOSITION

4

L.V. DE YONG, M. FITZGERALD AND [illegible]

MATERIALS RESEARCH LABORATORY

DSTO

METHODS FOR IMPROVING THE FLOWABILITY OF A PERCUSSION PRIMER COMPOSITION

L.V. de Yong, M. Fitzgerald and B. Whiffen

MRL Technical Report
MRL-TR-89-32

ABSTRACT

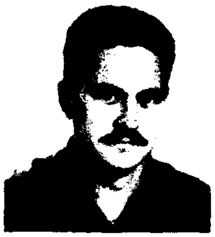
A vibrating hopper was used to evaluate and determine methods for improvement of the flowability of the percussion primer composition MRL(X) 408. The flowability was enhanced by granulation using both water and binder systems and using flow modifiers (silicon dioxide). Addition of binders reduced the sensitivity of the composition and, when filled into primers, increased the value of peak pressure and the rise time to peak pressure.

Published by DSTO Materials Research Laboratory
Cordite Avenue, Maribyrnong, Victoria 3032, Australia
Telephone: (03) 319 3887
Fax: (03) 318 4536

AR No. 005-734

2

AUTHORS



Leo de Yong graduated BAppSc (Chemistry) in 1977 from University of Melbourne. He worked for ICI Australia (Explosives) and Royal Melbourne Institute of Technology before joining MRL in 1982. His work has focussed on pyrotechnics and their applications.

Mark Fitzgerald joined MRL in 1978 and has worked in both the explosive and pyrotechnic areas. He is currently working on the thermal analysis of energetic materials.

Brian Whiffen joined MRL in 1971. He has worked exclusively on pyrotechnics, principally the development of novel pyrotechnic devices.

CONTENTS

METHODS FOR IMPROVING THE FLOWABILITY OF A PERCUSSION PRIMER COMPOSITION

1. INTRODUCTION

An important requirement in automatic powder filling systems is for the powder or granular material to possess uniform and free flowing properties. The powder must possess the ability to flow, for example, from a storage vessel into the required container in a manner which results in a reproducible mixture of ingredients and filling weight and at an acceptable production rate. These requirements are particularly important when the dry powder is an energetic material. Production operations involving energetic materials are frequently conducted remotely to reduce the potential hazards to personnel. However, if an energetic dry powder does not flow adequately, filling operations must be conducted manually, increasing the hazard to personnel and the cost of production. A second requirement, alluded to above, is that mixtures must retain integrity and not separate into individual components.

In 1980, Bentley and Elischer [1] developed a pyrotechnic percussion primer composition, designated MRL(X) 408, based on boron, lead oxide and tetracene (Table 1). This composition has a number of advantages over standard primers:

(i) percussion primers filled with MRL(X) 408 exhibit superior ability to ignite pyrotechnic compositions [2];

(ii) ignition results in low gas output, enabling use in hermetically sealed delay systems;

(iii) it is a simple three component mix unlike many currently used compositions.

Its major disadvantage, however, is that it has poor flowability which prohibits the primer being filled automatically using existing hardware, i.e. the primer must be hand filled, significantly increasing the production cost and the manufacturing hazard.

A study was undertaken at MRL to overcome this problem. Both the rheology of the primer composition MRL(X) 408 and methods for improving its flowability for use in an automatic filling process were examined. The results of the study are described in this report.

2. POWDER FLOW

When a powder is subjected to a continuous stress, it will deform elastically, start to yield and eventually fail completely. Deformation may then occur and flow begins [3]. In the case of flow from a hopper the continuous stress is simply due to gravity forces acting on the powder and the resistance to flow is broadly determined by the nature of the powder.

Considerable effort has been expended over recent years to study the rheology of powders, particularly flow from bins and hoppers [4-8]. These studies identified a number of factors that influence the flow rate of powders; the spatial arrangement of the particles, the particle size and shape, and interparticle forces. Interparticle forces are dependent to some extent on the previous parameters and fall into several categories.

(i) Mechanical forces and plastic welding due to the presence of rough surfaces or irregular shaped particles being interlocked then undergoing elastic deformation if a large enough force is applied to the particles.

(ii) Thin surface films due to adsorbed water or vapours which reduce the particle surface energy, contaminate the particle surface and reduce interparticle forces. Thicker films have significant surface tension and generate a large cohesive force.

(iii) Solid bridges between particles due to direct or secondary interactions such as chemical reactions, presence of binders and mineral bridges.

(iv) Molecular surface forces such as Van der Waals forces, dipole-dipole interactions etc.

(v) Electrostatic surface forces.

In terms of a powder flowing from a hopper, there are also several practical design factors that influence the particle flow. For flow through a circular orifice, the mass flow rate is dependent not only on the particle characteristics but also on the hopper diameter, the orifice diameter, the slope of the hopper wall and the quantity of material in the hopper. Of these, the quantity of material in the hopper has a negligible effect on flow rate as do wall effects if the hopper diameter is greater than 2.5 times the orifice diameter [6]. If the orifice diameter is less than six particle diameters across, then the flow may become intermittent and unreproducable as stable arches form over the orifice. These can usually only be broken by vibration [9].

Many workers have attempted to define the mass flow rate of particles from hoppers in terms of the particle and the hopper characteristics. The most successful of these is the Beverloo equation [10]:

$$W = C\rho g^{1/2} (D_o - kd)^{5/2}$$

where
- W = mass flow rate
- C = constant
- ρ = density
- D_o = orifice diameter
- k = a constant which is particle shape dependent
- d = particle diameter

For conical hoppers where the effect of wall inclination needs to be considered, a multiplicative factor is proposed [11]:

$$F(\alpha, \chi) = f(\tan \alpha)^{-0.35}$$

where α is the angle of inclination of the hopper wall to the vertical.

The problem with these equations is that they begin to break down for fine materials (< 500 μm) and flow difficulties become acute for particles < 100 μm. This behaviour is shown in Figure 1. In the final analysis, poor powder flow occurs with fine powders of irregular shape because of interparticle forces of attraction; the smaller the particle size, the greater the number of particle-particle contacts and the more irregular the shape, the greater particle interlocking.

Modification of the flow behaviour of a group of particles can therefore be accomplished by a number of strategies.

(i) Increasing the particle size, typically by agglomeration or granulation.

(ii) Increasing the density of the powder.

(iii) Increasing the diameter of the orifice through which the powder flows.

(iv) Reducing the magnitude of the interparticle forces of attraction using glidants or flow conditioners.

Flow conditioners are finely divided solids (diameter up to several microns) that are added to a host powder to improve its flowability and inhibit caking. The conditioner is usually a chemically inert substance belonging to one of the following groups - silicates, silicon oxide, stearates, talc, starch, phosphates. Most are insoluble in water and are effective in concentrations up to about 2%. Conditioners affect the flowability via several mechanisms. Since the conditioner particle adheres to the surface of the host particle, physical separation between the host particles occurs with a consequent reduction in interparticle interactions. The presence of conditioner particles may neutralise electrostatic charges or molecular attractive forces especially with low surface coverage. The conditioner particles may also pack around irregular shaped particles acting as a form of lubricant and reducing interparticle friction. Finally, many conditioners are hydrophilic and compete with the host powder for water, reducing the occurrence of liquid surface films on the host and thus the incidence of liquid bridging between host particles.

3. EXPERIMENTAL

3.1 Apparatus

Several methods have been employed to measure the flowability of powders, ranging from simple tests to measure the mass of material falling through an orifice to the angle of repose and shear cells [11]. Given the nature of the material under study, a shear method could not be used because of the sensitiveness of the material to mechanical stimuli, ie inducing rapid exothermic decomposition under shear. The angle of repose, although appropriate for free flowing materials, is inappropriate for poor flowing materials as it is rarely possible to measure a single unique angle. The flowability was determined using the technique of mass flow through an orifice using the apparatus shown in Figure 2. The eccentric weight on the air motor resulted in a horizontal displacement of the metal cone by 1.00 mm at a vibration frequency of 1700 rpm. The design of the metal cone was based on the Australian Standard Test Method D1755-81 for determining the flow rate of plastic materials. The cone angle was fixed at 20° and the orifice diameters were 2.1 mm and 3.0 mm. The smaller diameter corresponds to the diameter of the dies used in the current automatic filling system used for percussion primers at Munitions Filling Factory (MFF), St Marys.

Most of the initial testing was conducted using the composition B/Pb_3O_4 (10:90) because it is much less sensitive than MRL(X) 408.

3.2 Materials

The samples of boron and red lead oxide (Pb_3O_4) were obtained from MFF St Marys. The boron was a washed technical grade material (min. 84% purity) with a nominal average particle size of 0.5 - 2.0 μm. Particle sizing measurements conducted with a Malvern 2600 particle sizer indicated that the average size was sub-micron, a result confirmed by scanning electron microscopy (Figure 3(a)) [12].

The Pb_3O_4 was jointing grade with a purity of between 72 and 90%, the residue being predominantly PbO. The nominal mean particle size was 2.5 μm, confirmed by scanning electron microscopy (Figure 3(b)).

The tetracene was type RD 1336 manufactured at MRL using standard techniques. The mean particle size was 86.2 μm.

The magnesium, calcium and zinc stearate, and the talc flow modifiers were all technical grade and supplied by Ajax Chemicals or BDH Chemicals. The silicon dioxide modifiers were Cab-o-sil TS720 (Cabot Corp. USA), Aerosil R972 (Degussa, FRG) and Wacker HDK H15 (Wacker-Chemie GMBH). All were hydrophobic and had an average particle size below 1 μm.

3.3 Preparation of Compositions

3.3.1 B/Pb_3O_4 and MRL (X) 408

The pyrotechnic composition of boron and lead oxide (10:90) was prepared in the standard way by sieve sizing of the ingredients then mixing in a Jelly Mould mixer for 60 min to produce a homogeneous blend. The tetracene was remotely mixed with the boron and the lead oxide using a Jelly Mould mixer (1 h mixing time at 13.5 rpm). Batch sizes were restricted to 30 g because of the sensitive nature of the composition.

3.3.2 Incorporation of Flow Modifiers

The flow conditioners were incorporated into the mix by firstly sieve mixing 10% of the required modifier mass with the boron and the remaining 90% with the lead oxide. The two components were then dry mixed separately in a WAB Turbula mixer for 25 minutes. The two components were then combined and mixed in a Jelly Mould mixer for 60 min.

3.3.3 Granulation

Granulation was conducted by placing 30 g of composition in a crucible with sufficient solvent to form a paste. After hand mixing to achieve consistency, the paste was allowed to stand to evaporate excess liquid. When the composition had reached the consistency of "damp sand", it was forced through a British Standard Sieve (BSS) using a rubber bung. The resulting granules were oven dried at 90°C. The three granulation procedures are detailed below.

Water granulation:

Mix water (about 13 mL) with B/Pb_3O_4 (100 g) then granulate through sieve.

Gum arabic:

First make up a gum arabic (acacia gum) solution with H_2O, eg 1% = 1 g gum arabic powder mixed with 100 mL H_2O. Then take 15 mL gum arabic solution, 100 g B/Pb_3O_4, mix together, granulate through the sieve and dry. In the text, granulation with 1% gum arabic solution means 100 g Pb_3O_4/B composition with 15 mL of 1% gum arabic solution, i.e. 100 g B/Pb_3O_4 + 0.15 g gum arabic in the granulated system after drying. "5% Gum arabic" is similarly prepared from 15 mL of 5% solution.

Nitrocellulose (NC) granulation:

Make up an NC solution by dissolving RD 1198B NC lacquer in acetone, then mix with the B/Pb_3O_4, granulate and dry. In the test a 1% granulation is 1 g RD 1198B dissolved in an adequate amount of acetone added to 99 g B/Pb_3O_4. 5% NC is 5 g RD 1198B dissolved in acetone added to 95 g B/Pb_3O_4.

4. RESULTS

Improvement of the flow behaviour of the composition MRL(X) 408 concentrated on two areas: the addition of flow modifiers to the mixture or alteration of the particle size of one or more of the components of the composition. Ideally, the improved composition should flow freely from the metal cone in a similar manner to a material currently used in existing automatic filling systems. Two materials were chosen for comparison: antimony sulphide, Sb_2S_3, and PA101, a currently used primer composition. The flow rates of both these compositions and MRL(X) 408 were measured using the apparatus shown in Figure 2. The results are detailed in Table 2.

Clearly, the primer composition MRL(X) 408 exhibits poor flow properties when compared to Sb_2S_3 and PA101. Examination of a scanning electron micrograph for Sb_2S_3 shows that its excellent flow rate is due to its large mean particle size (150–200 μm), its regular particle shape (Figure 3(c)) and the absence of fine particles.

The mass flow rates were determined by averaging between five separate tests. Typical variation in repeated tests is shown in Figure 4.

4.1 Flow Modifiers

The mass flow rate of B/Pb_3O_4 with a range of percentages of the silicon dioxide flow modifiers is shown in Figures 5 and 6. All other flow modifiers resulted in diminished flow due to formation of stable arches which constantly blocked the flow. Vibration was not successful in causing flow and these materials were not examined further.

The results in Figures 5 and 6 show that the addition of silicon dioxide increases the flow rate of the B/Pb_3O_4 for both 2.1 mm and 3.0 mm orifice diameters. As expected, the flow rate is greater with the 3.0 mm orifice. In all cases, the maximum flow rate occurs with the addition of 0.5% modifier and further additions decrease the flow rate. Although there is only a slight difference, using the 2.1 mm orifice, between the flow rates produced by the three modifiers, the difference becomes more pronounced as the orifice diameter increases to 3.0 mm. For both orifice diameters Cab-o-sil shows the greatest efficiency in increasing the flow rate of the B/Pb_3O_4.

An alternative indicator of flowability is the mass of material which will flow through the orifice without vibration when the cone is filled and before flow ceases due to formation of stable arches. Figure 7 shows that the addition of flow modifiers to B/Pb_3O_4 increases this initial mass flow with Cab-o-sil exhibiting the best performance.

The flow rate through the 2.1 mm orifice for B/Pb_3O_4 + 0.5% Cab-o-sil, 4.0 g min^{-1}, is still significantly below that for Sb_2S_3 or PA101 (Table 2). Further improvement is therefore necessary.

4.2 Improvement in Particle Size

Flow problems occur with small particle size material (see Introduction and Figure 1). The particle size of both the boron and the Pb_3O_4 is small, and falls into the region where poor flow would be expected. Improvements in flowability can potentially be achieved by increasing the particle size of these materials. Options for achieving this include addition of a binder and sizing through an appropriate sieve, solvent granulation of the boron and lead oxide, or chemically increasing the particle size of one component.

The Pb_3O_4 also is present as small particles which may present toxicological problems during the mixing operation; the Pb_3O_4 may become suspended in the air as a dust, and inhalation may occur unless safety precautions are undertaken. This problem may be significantly reduced by increasing the particle size of the Pb_3O_4.

4.2.1 Solvent Granulation

Wet or solvent granulation of a pyrotechnic composition involves the addition of a liquid medium to partially dissolve at least one of the components in the composition. The dampened composition is forced through a sieve and the resulting granules are dried, depositing the partially soluble material on the surface. However, neither the boron nor Pb_3O_4 components of MRL(X) 408 are soluble in most common solvents, but addition of a solvent could bind the particles together through the dissolution of small amounts of impurities in the boron (Mg, B_2O_3). Subsequent heating evaporates the solvent leaving a larger particle size granule.

The results for the mass flow rate of B/Pb_3O_4 granulated using water, ethanol and acetone with a range of sizing sieves (BSS 10 to BSS 65) are shown in Figure 8. The results show that solvent granulation increases the mass flow rate of the composition; water gave a superior product compared to ethanol or acetone. The maximum flow rate of 14.0 g min^{-1} occurs with the product which has been granulated through a BSS 18 sieve. This is a significant improvement over that for B/Pb_3O_4 with 0.5% Cab-o-sil and is similar to the flow rate of PA101 (Table 2).

The major problem with these granulations are their low mechanical strength caused by of their poor dissolution in the solvent, the low level of impurities and the small number and low strength of the particle to particle bonds. Figure 9 shows the change in the mass flow rate of the BSS 18 solvent granulated B/Pb_3O_4 with repeated passes through the hopper. This procedure gives an indication of granule strength. The granules formed using ethanol break up markedly, the flow rate decreasing from 9.8 g min^{-1} to 5.3 g min^{-1} after only four passes. The granules formed using water or acetone show a much smaller decrease in flow rate (ca. 5%) with repeated testing.

Granulation using tetracene was also examined. Tetracene was dissolved in formic acid, B/Pb_3O_4 added, then the tetracene was precipitated out with H_2O. The tetracene was easily precipitated out either slowly or rapidly but with only 5% in the total composition mass, it made no effect on the flowability even though there was some evidence of the tetracene coating the B/Pb_3O_4 mix.

4.2.2 Granulation using Binder

Adding binder in a solvent to the composition is an alternative technique; the composition is then dried and granulated as before with the binder providing the mechanical strength. The major disadvantage of this technique is that the binder could substantially modify the performance and/or the sensitivity of the composition. Gum arabic and nitrocellulose lacquer (RD 1198B) were examined as binders; both are commonly used in pyrotechnics. Percentages referred to in the text are defined in Section 3.3.

4.2.2.1 Gum Arabic (Acacia Gum) Binder

The flow rate of B/Pb_3O_4 granulated with gum arabic solution using a range of sizing sieves is shown in Figure 10. The change in flow rate is similar to that observed with solvent granulations (Figure 8), the maximum flow rate being for a material granulated with a BSS 18 sieve. The maximum flow rate is for the composition prepared from 5% binder solution; this is approximately 15% greater than for the water granulated product.

Evaluation of the mechanical strength of the granulation by repeated passes through the orifice is presented in Figure 11. Decrease in flow rate for B/Pb_3O_4 prepared from gum arabic solutions of less than 1% is due to the breakdown of the granules and decrease in effective particle size.

The amount of material which flowed through the hopper without vibration is presented in Figure 12. The masses observed were very low; only 0.0 - 0.1 g compared to 0.5 g to 5.0 g for the flow modified materials (Figure 7). Both the gum arabic granulated and the flow modified sample exhibited increased initial flow through the orifice with increasing sieve size (increasing particle size).

4.2.2.2 Nitrocellulose (NC) Binder (RD 1198B)

The mass flow rate of B/Pb_3O_4 granulated with 1% and 5% RD 1198B in acetone using a range of sizing sieves is presented in Figure 13. As for all the previous granulations, flow occurs when the sieve size exceeds BSS 10 and increases with increasing sieve size. For the range of sieves examined, use of 5% NC produces granules that have superior flow rate to those produced from 1% NC. For the granules from 5% NC, the maximum flow rate occurs when a BSS 36 sieve is used for granulation; the flow rate of 15.4 g min^{-1} is comparable to PA101 (Table 2).

The change in the mass flow rate of B/Pb_3O_4 granulated with 1% and 5% NC produced by repeated passes through the orifice is shown in Figure 14. Both formulations show minimal change in flow rate indicating good mechanical strength of the granules.

4.2.3 Manufacture of Large Particle Size Pb_3O_4

The results in the previous sections clearly demonstrate that an acceptable mass flow rate can be achieved by increasing the particle size of the composition. An alternative to granulation is to chemically increase the particle size of the major component of the composition, ie Pb_3O_4. Large particle size PbO was prepared by aqueous precipitation ($Pb(NO_3)_2$ + NaOH), then was heated at 470°C for several hours in a stream of air to convert to Pb_3O_4. The particle size achieved was approximately 70 μm and the unvibrated mass flow rate was 35.4 g min^{-1}. However analysis using X-ray diffraction indicated poor conversion to Pb_3O_4 [12]. The problem of conversion to Pb_3O_4 ruled out this method as a viable solution to production of modified MRL(X) 408.

4.3 Sensitivity and Performance

Although improvements in the flowability of MRL(X) 408 can be achieved by the methods discussed above, the improved formulation must exhibit similar sensitivity to initiation and similar performance to the original formulation.

4.3.1 Sensitivity

MRL(X) 408 is the filling in the percussion primer M42F1 and is consequently designed to be particularly sensitive. The sensitivity of a range of modified MRL(X) 408 compositions was determined in both filled primer hardware and as loose powders.

The sensitivity of the compositions filled into primers was determined using a free falling striker of a similar design to the strikers used in fuzes [1]. Preliminary determinations were conducted at a number of drop heights (ie striker energies) to obtain an approximate 50% ignition probability. The striker height was then varied in intervals of 10% of this fire level. Each experiment was assessed as either a fire or no fire and at least 15 primers were tested for each composition. The results were analysed using the Bruceton method [14] and represent the 50% ignition energy. The results presented in Table 3 show that the 50% ignition energy is increased by the addition of flow modifiers and binders, ie the sensitiveness of the compositions has decreased. The large particle size "Pb_3O_4" produced from PbO exhibited poor sensitivity due to the low purity; PbO is much less effective in these compositions.

The sensitiveness of the loose compositions was determined using a range of standard tests. Temperature of Ignition (T of I) using a heating rate of 5°Cmin^{-1}, Powder Impact Sensitiveness (F of I) using a Rotter Apparatus (5 kg drop mass) and Electrostatic Spark Test [13]. The results are detailed in Table 4 and show a slight decrease in sensitiveness to impact and a slight increase in temperature of ignition with granulation or addition of binders. This confirms the decrease in sensitivity observed with filled primers. Sensitiveness to spark remains unaffected. The significant increase in sensitiveness (decrease in F of I and T of I) from addition of tetracene can clearly be seen; although only 5% is present, it is the component which determines response.

4.3.2 Performance

Primers containing MRL(X) 408 generate predominantly condensed reaction products, leading to a low pressure upon ignition. Modification of the MRL(X) 408 formulation by incorporation of ingredients which produce gas during the ignition process may affect primer performance by altering the peak pressure and the functioning time to peak pressure.

Several primers filled with modified compositions were fired into a fixed volume (41.6 cm^3) and the pressure/time profile recorded. The values of P_{max} and the rise time to P_{max} are listed in Table 5. The results show that the modifications to the composition cause a negligible change in P_{max} but there is a definite increase in the rise time to P_{max}. This is most probably due to the additives (gum arabic, Cab-o-sil) slowing down the rate of the B/Pb_3O_4 combustion reaction.

5. DISCUSSION

Improvement in the flowability of B/Pb_3O_4 may be achieved by the addition of flow modifiers based on silicon dioxide but not by the addition of talc or stearates. Of the silicon dioxide systems which were examined, Cab-o-sil showed the largest effect on the flow rate of B/Pb_3O_4 relative to use of Wacker HDK H15 and Aerosil R972 (Figures 5 and 6). The flow rate data for a number of modified compositions are listed in Table 6. The improvement in the flow rate with the addition of 0.5% Cab-o-sil is significantly less than can be achieved by some of the binders, or by granulation. In addition, the decrease in bulk density caused by addition of silicon dioxide introduces problems for storage, handling and pressing. Achievement of a uniform blend of B/Pb_3O_4/silicon dioxide requires that the silicon dioxide be mixed (sieve or turbula) with each ingredient; mixing all ingredients together does not produce a homogeneous blend. Flow modifiers do, however, have the advantage of enhancing the initial flow through the hopper without vibration. Initial flow of mixes incorporating silicon dioxide is 1-4 g compared to 0.01 - 0.1 g for gum arabic granulations. A primer contains only 0.02 g of composition, therefore it is possible that it may be automatically filled without vibration using this feature of the flow modifier effect, although reproducibility would need to be thoroughly assessed.

The results in Table 6 show that granulation with water, gum arabic solution or NC significantly improves the flowability of the B/Pb_3O_4 composition from 1-1.5 g min^{-1} to 13-16 g min^{-1}. As noted earlier (4.2.1) solvent granulation typically involves dissolution of one or more of the components of the composition. However, neither B nor Pb_3O_4 are appreciably soluble in any of the solvents used here. In this case, part of the solvent is retained on the particle surface which then forms hydrogen bonds with the adjacent solvent coated particles. There will also be slight mechanical interlocking of the particles. Water of crystallisation will be retained on the water granulated material, even after drying, producing stronger hydrogen bonding than with acetone or ethanol. The granules formed from the water process should then be stronger than those formed using acetone or ethanol. This is verified by the results in Figure 9, where the flow rate of the water granulated product is greater than for ethanol or acetone granulation and remains constant with repeated testing. However, the granules formed by water granulation break up when mechanically mixed with tetracene, reducing their particle size and consequently their mass flow rate.

The use of a binder in the granulation process is expected to improve flowability (similar to solvent granulation) and increase the mechanical strength of the granules. Table 6 shows that the flow rate of B/Pb_3O_4 is increased, relative to ungranulated B/Pb_3O_4, when granulated with gum arabic solution (1%, 5% and 10%) and NC (1% and 5%). It is interesting to note that the flow rate is similar to that observed for water granulated B/Pb_3O_4. However, the granules usually break up when mixed with tetracene, reducing their particle size and flowability; the exceptions to this behaviour are the granulations using 10% gum arabic solution and 5% NC. This indicates that a minimum level of binder is required to ensure sufficient granule strength. The granulation with 1% NC may also be considered to be an exception as it retains its high flow rate after mixing with tetracene but then breaks down when the Cab-o-sil is added (mixing was conducted in a jelly mould mixer for 60 minutes to achieve homogeneity).

Although the flowability may be enhanced by the treatments outlined above, their ignition sensitivity and performance should not be adversely affected. The granulation process or the addition of a binder reduces impact sensitiveness (F of I increases) and thermal sensitivity (T of I increases) (Table 4). This result is expected and is similar to the desensitizing action of soft binders on secondary explosives subjected to high shear or impact loading [15].

The sensitivity of the compositions is not affected by the addition of 0.5% of the flow modifier Cab-o-sil (F of I and T of I unchanged). Cab-o-sil acts to reduce interparticle forces and thus to separate particles in a loose powder. It has been observed at MRL that flow modifiers may increase the sensitiveness of a pressed composition to impact ($Al/KClO_4$, F of I decreased from 80 to 65 with flow modifier changed from 0% to 2%). This is due to the relative hardness of the flow modifier (SiO_2) compared to the Al and the $KClO_4$; the flow modifier is significantly harder than either component and so effectively acts as a grit, sensitizing the composition to impact. For B/Pb_3O_4, boron is harder than SiO_2 and so no sensitizing effect is noted.

Addition of 5.0% tetracene to the B/Pb_3O_4 composition increases sensitivity as expected. The sensitizing action of tetracene is well known [16-18].

The sensitivity of the primers must also be maintained when filled with the modified formulations. The 50% ignition energy values for filled primers (Table 3) show similar behaviour to the sensitivity data in Table 4; increasing the binder content increases the ignition energy. Table 3 also contains approximate figures for the upper 95% confidence limit for the 99% probability ignition energy which were derived from the Bruceton test data.

The striker from a standard mechanically initiated device (M49A1 Trip Flare) was calculated to typically deliver an impact energy of 200-250 mJ. Comparison between this figure and the 99% ignition energy figures shows that the use of 1% NC or 5% gum arabic solution in the formulations produces primers with acceptable performance. The addition of 0.5% Cab-o-sil also gives primers with sensitivity within the striker energy limits. However, treatment with 10% gum arabic solution gives primers with decreased sensitivity which would be likely to have significant malfunction rates whilst 5% NC and PbO/Pb_3O_4 are unacceptable as their energy requirements are greater than that available from the striker.

Initial evaluation of the performance of the compositions assembled into primers was based on the premise that any increase in the peak pressure may decrease performance in igniting pyrotechnics [2,18]. Table 5 shows that the addition of binders or flow modifiers increases the peak combustion pressure. As such the ignition performance of the primers could be expected to be lower than the standard M42F1 primer although no experiments were conducted to verify this behaviour. However, the rate of combustion (which is inversely proportional to the rise time to P_{max}) exhibits a large decrease with the addition of a binder, the rise time increasing from 11.9 ms to an average of 25 ms. This fact may not affect the primer performance but may affect the functioning time of stores where a high accuracy delay is a component in the ignition train.

We have shown that an improvement in the flowability of the MRL developed primer formulation MRL(X) 408 may be achieved by four processes:

(i) addition of 0.5% of the flow modifier Cab-o-sil
(ii) granulation with water
(iii) granulation with 5% or less gum arabic
(iv) granulation with 1% or less NC.

The best process is (iv). The limits on NC and gum arabic content are necessary to maintain the primer sensitivity and to minimise the gas pressure from firing of the primer.

A group of formulations (Table 7) were trialled in the automatic filling line at MFF St Marys, Sydney. The compositions were mixed at MRL then sent to MFF where the tetracene was added using a jelly-mould mixer. The water granulated sample and that containing Cab-o-sil visually exhibited poor flowability and homogeneity and were not used for further testing. The other compositions were volumetrically loaded into M42 primer cups using the 1000 cap tray production facility. The compositions were assessed by noting ease and consistency of fill in both the M42 charge plate and the primer cup. Those which were considered satisfactory were pressed and anvils added. The filled caps then underwent limited sensitivity and functioning tests.

The 1% NC/BSS 65 composition showed a definite improvement over the existing formulation, however only approximately 75% of the charge cavities were filled. Loading the caps from the charge plate was unsuccessful; very few of the caps were loaded and the height of fill varied considerably. The 1% NC/BSS 36 composition showed a significant improvement but the cap fill height showed excessive variation and only 20% of the caps were filled from the charge plate.

The 1% gum arabic composition successfully filled the charge plate and the caps. However, due to the greater bulk density of the composition, the caps were underfilled. Using a 7.62 calibre charge plate (larger volume) ensured an even cap fill but they were overcharged. Using a 0.303 charge plate, the caps were slightly overfilled but the fill heights were even. Similar results were obtained for the 5% gum arabic composition.

Primers with 1% gum arabic filling using the 7.62 caiibre charge plate and primers with 5% gum arabic filled using the 0.303 calibre charge plate were subjected to sensitivity and functioning tests. Both primers failed these tests almost certainly due to the desensitizing effect of the high fill height.

The primer filling system uses a wiper mechanism to fill the cap tray with the composition. All the compositions showed some granule breakup due to this wiper action, although the 1% and 5% gum arabic compositions performed better than the others.

6. CONCLUSION

Enhanced flowability of the M42F1 percussion primer composition may be achieved by either solvent granulation, addition of a flow modified or by granulation with a binder. Evaluation of the modified compositions using production equipment showed that compositions granulated with NC or gum arabic binders performed superior to the other compositions. However, problems due to the composition density would require re-working the charge plate so that the charge volume closely matches the composition bulk density.

7. REFERENCES

1. Bentley, J.R. and Elischer, P.P. (1980). Development of a gasless pyrotechnic cap (MRL Report MRL-R-776). Maribyrnong, Vic.: Materials Research Laboratory.

2. de Yong, L.V. and Wanat, E. (1986). A standoff test to determine the ignitability of pyrotechnics and the ignition effectiveness of pyrotechnic igniters (MRL Report MRL-R-998). Maribyrnong, Vic.: Materials Research Laboratory.

3. Ashton, M.D., Cheng, D.C-H., Farley, R. and Valentin, F.H.H. (1985). Rheologica Acta, **4**, 206.

4. Burak, N. (1966). Chemicals for improving the flow properties of powders, Chemistry & Industry., May, 844.

5. Parfit, G.D. and Sing, K.S. (ed), (1976). Characterization of powder surfaces, London: Academic Press, p. 108.

6. Nedderman, R.M., Trozan, U., Savage, S.B. and Houslby, G.T. (1982). The flow of granular materials - I. Discharge rates from hoppers, Chemical Engineering Science, London : Pergamon Press, **37**, 1597.

7. Peleg, M. and Hollenbach, A. (1984). Flow conditioners and anticaking agents, Food Technology, 93.

8. Brown, R.L. and Richards, J.C. (1959). Transactions of the Institution of Chemical Engineers, **37**, 108.

9. Harwood, C.F. and Pilpel, N. (1969). The flow of granular solids through circular orifices, Journal of Pharmaceutical Pharmacology, **21**, 721.

10. Beverloo, W.A., Leniger, H.A. and de Velde, V. (1961). Journal of Chemical and Engineering Science, **15**, 260.

11. Jenike, A.W. (1964). Storage and flow of solids, Bulletin 123, Engineering Experimental Station, Utah State University, USA.

12. Silva, V. and Cullen, P. (1984). Materials Research Lab., unpublished results.

13. UK Sensitiveness Collaboration Committee No. 3 (1971). Explosives hazard assessment, Manual of Tests.

14. Culling, H.P. (1953). Statistical methods appropriate for evaluation of fuze-explosive train safety and reliability (NAVORD Report 2102). Whiteoak, MD: US Naval Ordnance Laboratory.

15. Dagley, I.J., Spear, R.J. and Nanut, V. (1987). High explosive moulding powders from RDX and aqueous polyurethane dispersions (MRL Report MRL-R-1062). Maribyrnong, Vic.: Materials Research Laboratory.

16. Spear, R.J. and Elischer, P.P. (1982). Australian Journal of Chemistry, **35**, 1.

17. Bowden, F.P. and Yoffe, A.D. (1958). Fast reactions in solids, Butterworths: London.

18. de Yong, L.V. (1988). Predicting the performance of percussion primers, Proceedings of 13th International Pyrotechnics Seminar, Colorado, USA.

Table 1 **Chemical Composition of MRL(X) 408**

Ingredient	Weight (%)	Median Particle Size (μm)	Bulk Density (Mg/m^{-3})
Boron (amorphous)	9.5	< 1	2.35
Red Lead Oxide	85.5	2.5	9.1
Tetracene	5.0	86.2	0.70

Table 2 **Mass Flow Rates of Standard Compositions through a 2.1 mm diameter Orifice**

Composition	Flow Rate (g min^{-1})	
	Vibrated	Unvibrated
MRL(X) 408	1.0-1.5	Nil
PA101 [a]	18-20	20-25
Sb_2S_3	37.2	41.1

a PA101 consists of monobasic lead styphnate (53%), Sb_2S_3 (10%), barium nitrate (22%), Al (10%), tetrazene (5%).

Table 3 **Ignition Sensitivity of MRL(X) 408 Type Compositions Filled into Standard Percussion Primer Hardware**

Composition	50% Ignition Energy (mJ)	Approximate 95% Confidence Limit for 99% Ignition Energy (mJ)
B/Pb_3O_4/Tetracene [a]	125.8	195
B/Pb_3O_4/Tetracene/10% Gum Arabic	145.4	215
B/Pb_3O_4/Tetracene/10% Gum Arabic/0.5% Cab-o-sil	184.4	255
B/Pb_3O_4/Tetracene/0.5% Cab-o-sil	134.0	205
B/Pb_3O_4/Tetracene/5% Gum Arabic/0.5% Cab-o-sil	128.7	210
B/Pb_3O_4/Tetracene/1% NC Lacquer	151.6	220
B/Pb_3O_4/Tetracene/5% NC Lacquer	177.4	250
B/"Pb_3O_4"/Tetracene [b]	> 200	> 280

a MRL(X) 408

b Large particle size Pb_3O_4 produced from PbO (see section 4.2.3)

Table 4 **Mechanical (Impact), Thermal and Electrostatic Sensitivity Data for MRL(X) 408 Formulations**

Composition	F of I [a]	T of I [b] (^{o}C)	Spark Sensitivity (J)
B/Pb_3O_4 (10:90)	25	360	Ignites 0.045
B/Pb_3O_4 (10:90) H_2O Granulated, BSS 18	35	381	Ignites 0.045
B/Pb_3O_4 (10:90) 1% Gum Arabic Granulated, BSS 36	35	373	Ignites 0.045
B/Pb_3O_4 (10:90) 5% Gum Arabic Granulated, BSS 18	30	390	Ignites 0.045
B/Pb_3O_4 (10:90) 10% Gum Arabic Granulated, BSS 18	35	390	Ignites 0.045
B/Pb_3O_4/Tetracene (9.5:85.5:5.0) [c]	10	145	Ignites 0.045
B/Pb_3O_4/Tetracene (9.5:85.5:5.0) 10% Gum Arabic Granulated, BSS 18	15	148	Ignites 0.045
B/Pb_3O_4/Tetracene/Cab-o-sil (9.45:85.05:5.0:0.5) 10% Gum Arabic Granulated BSS 18	20	138	Ignites 0.045
B/Pb_3O_4/Tetracene/Cab-o-sil (9.45:85.05:5.0:0.5) 5% Gum Arabic Granulated BSS 18	15	135	Ignites 0.045
B/Pb_3O_4/Tetracene/Cab-o-sil (9.45:85.05:5.0:0.5)	15	135	Ignites 0.045
B/Pb_3O_4/Tetracene/1% NC Lacquer (9.4:84.6:5:1)	20	136	Ignites 0.045
B/Pb_3O_4/Tetracene/5% NC Lacquer (9.0:81.2:5:4.8)	15	136	Ignites 0.045

a Figure of Insensitiveness relative to RDX = 80 as standard

b Temperature of Ignition at heating rate $5^{o}C\ min^{-1}$

c MRL(X) 408

Table 5 **Pressure/Time Data for Selected Percussion Primer Formulations**

Composition	Peak Pressure (kPa)	Rise Time to Peak Pressure (ms)
B/Pb_3O_4/Tetracene	31.5	11.9
B/Pb_3O_4/Tetracene/10% Gum Arabic	33.6	22.3
B/Pb_3O_4/Tetracene/10% Gum Arabic/Cab-o-sil	28.7	28.9
B/Pb_3O_4/Tetracene/5% Gum Arabic/Cab-o-sil	34.6	20.7
B/Pb_3O_4/Tetracene/Cab-o-sil	30.6	41.3

Table 6 **Flow Rates of MRL(X) 408 Type Compositions under Vibration**

	Flow Rate ($g\ min^{-1}$) [a]		
	B/Pb_3O_4	+ Tetracene	+ Tetrazene + Cab-o-sil
Standard			
B/Pb_3O_4 (10:90)	1-1.5 (4.0 [b])	1-1.5 [c]	6.6
Granulated Compositions			
H_2O granulation, BSS 18	14.0	4-4.5	6-7
1% Gum Arabic, BSS 36	13.5	2.2	4.5
5% Gum Arabic, BSS 18	16.3	5.2	6-8
10% Gum Arabic, BSS 18	13.5	16-18	18-20
1% NC, BSS 65	14.1	10.5	3.5
5% NC, BSS 36	15.4	18.0	22.8

a For comparison the primer composition PA101 has a flow rate of 18-20 $g\ min^{-1}$

b B/Pb_3O_4/0.5% Cab-o-sil

c MRL(X) 408

Table 7 Formulations Trialled on Automatic Filling Line

Composition	Binder/Solvent	Granulation Size[a]	Flow Modifier
boron/red lead oxide	1% nitrocellulose/ acetone	BSS 65	-
boron/red lead oxide	1% nitrocellulose/ acetone	BSS 36	-
boron/red lead oxide	Water	BSS 18	-
boron/red lead oxide	1% Gum Arabic/ water	BSS 18	-
boron/red lead oxide	5% Gum Arabic/ water	BSS 18	-
boron/red lead oxide	-	-	Cab-o-sil (0.5%)

a British Specification BS 410

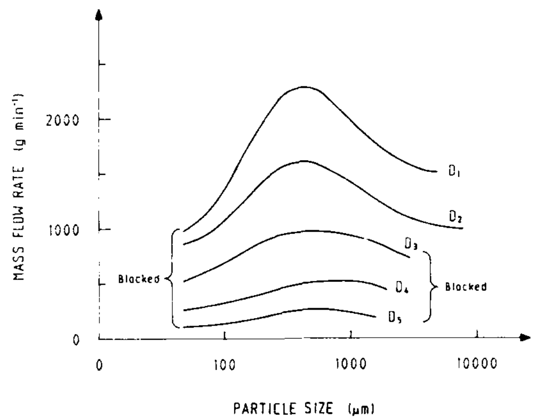


Figure 1 ***Effect of Particle Size on the mass flow rate of a powder; orifice diameter $D_1 > D_2 > D_3 > D_4 > D_5$.***

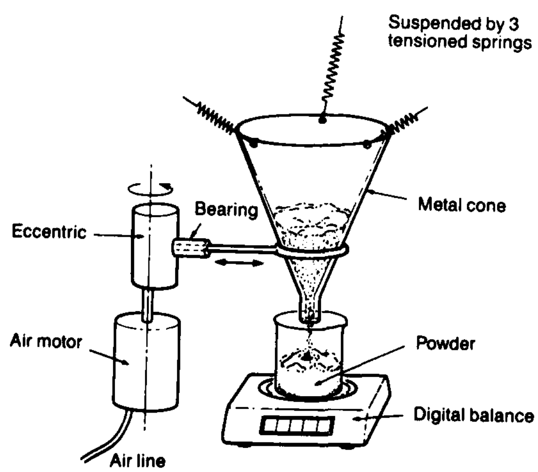


Figure 2 Vibrating hopper used to measure the mass flow rates of powders.

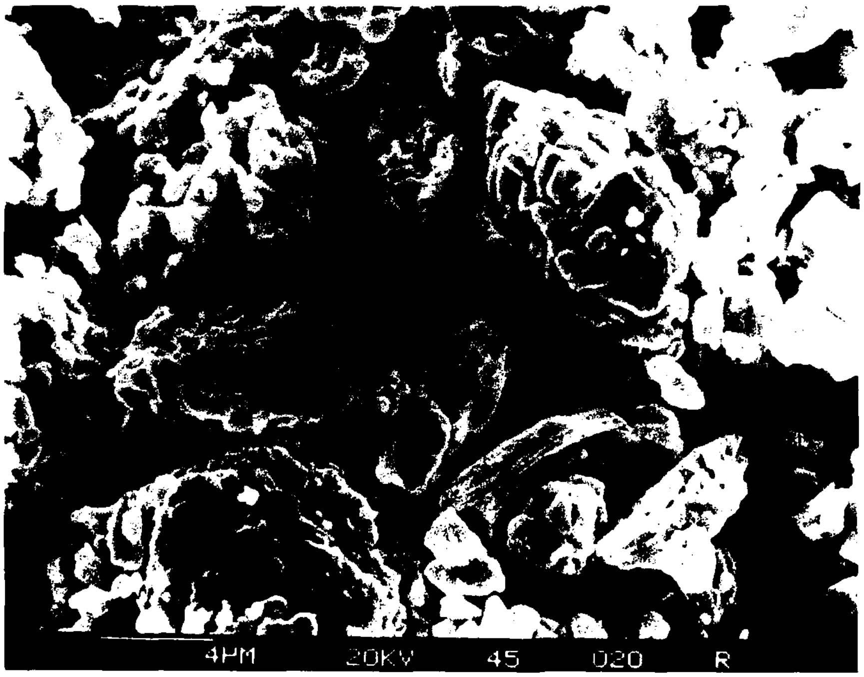


Figure 3 (a) Scanning Electron Micrograph of Amorphous Boron

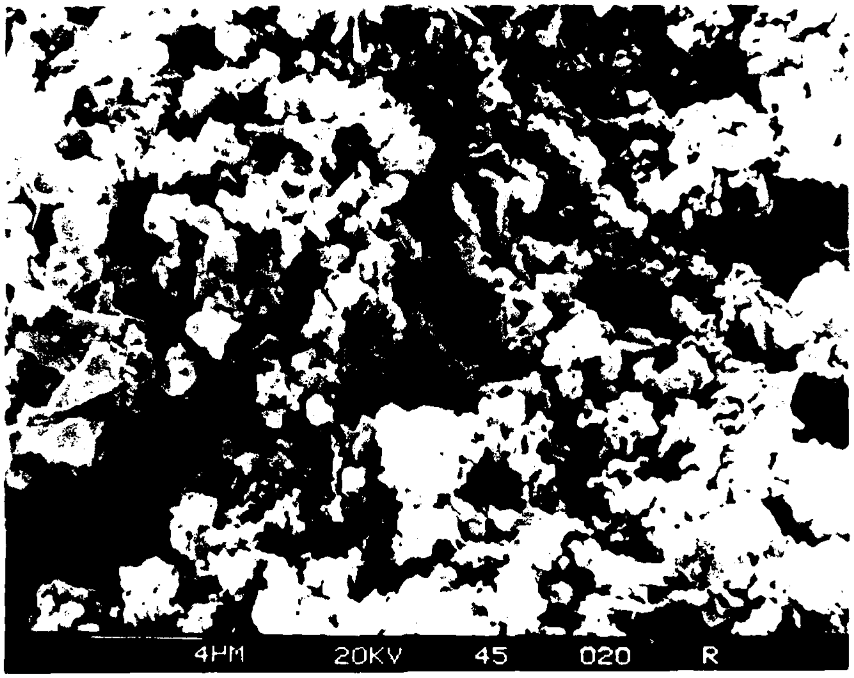


Figure 3 (b) Scanning Electron Micrograph of Red Lead Oxide (Pb_3O_4)

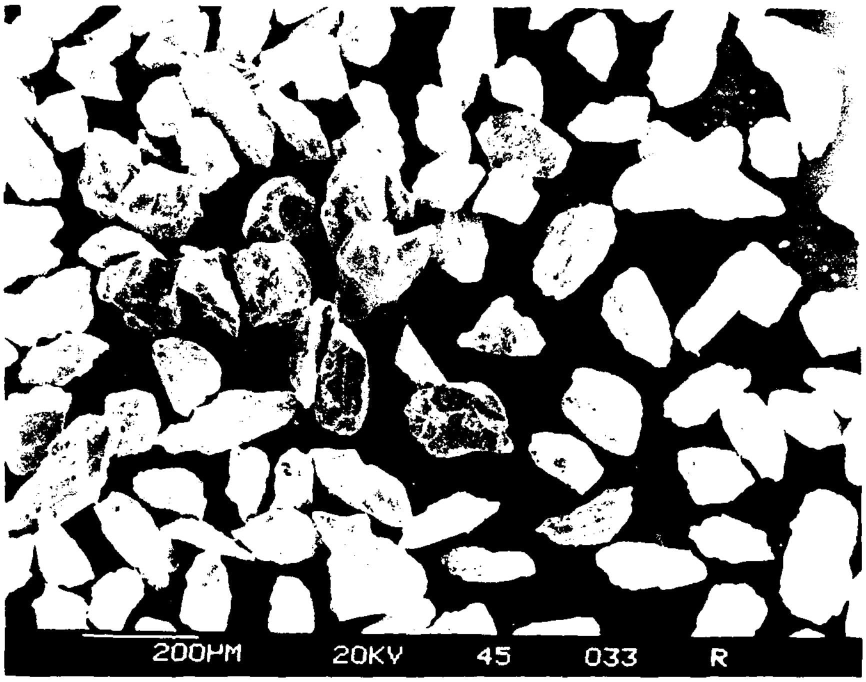


Figure 3 (c) Scanning Electron Micrograph of Antimony Sulphide (Sb_2S_3)

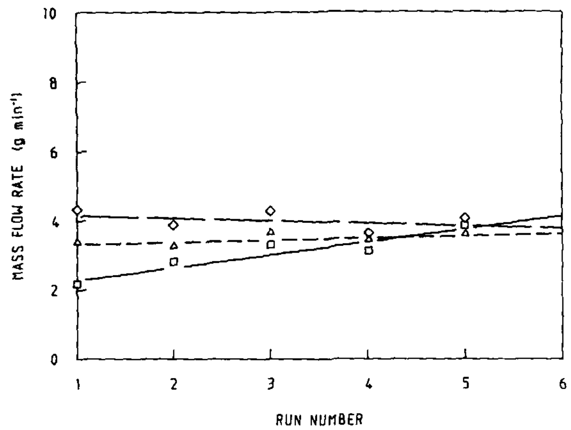


Figure 4 — *Change in mass flow rate with repeated testing of B/Pb_3O_4 (10:90) with 0.5% flow modifier; △ Wacker HDK H14, ◇ Cab-o-sil 72720, □ Aerosil R972.*

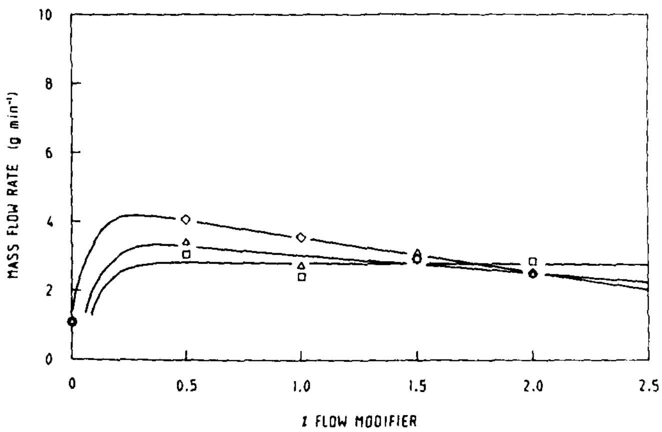


Figure 5 — *Mass flow rate of B/Pb_3O_4 (10:90) through a 2.1 mm orifice with selected flow modifiers; △ Wacker HDK H15, ◇ Cab-o-sil 75720, □ Aerosil R972.*

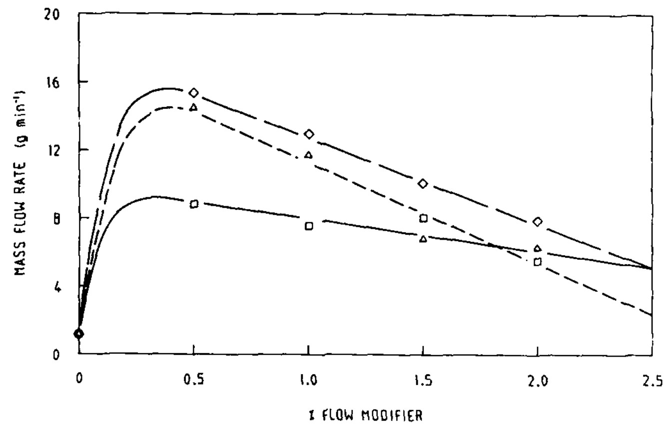


Figure 6 **Mass flow rate of B/Pb_3O_4 (10:90) through a 3.0 mm orifice with selected flow modifiers; △ Wacker HDK H15, ◇ Cab-o-sil 75720, □ Aerosil R972.**

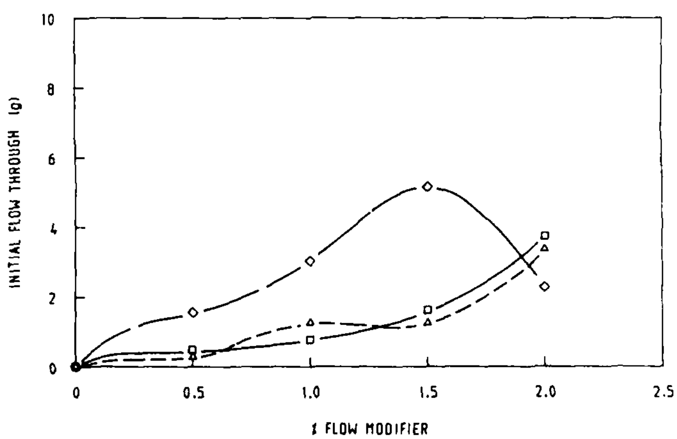


Figure 7 **Initial mass flow of B/Pb_3O_4 (10:90) with selected flow modifiers before hopper vibration; △ Wacker HDK H15, ◇ Cab-o-sil 75720, □ Aerosil R972.**

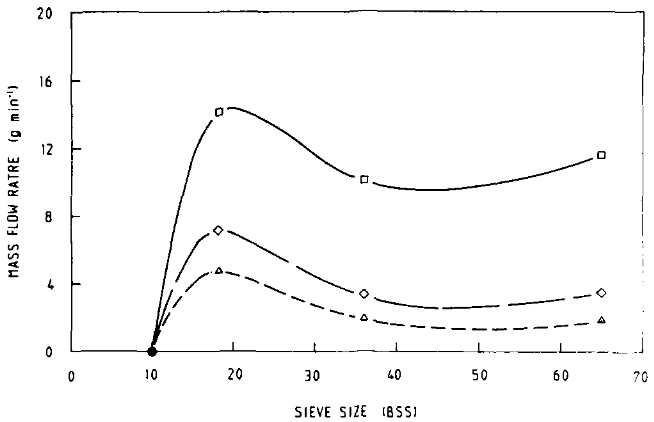


Figure 8 **Mass flow rate of B/Pb_3O_4 (10:90) granulated through selected sieves using several solvents; △ acetone, ◇ ethanol, □ water**

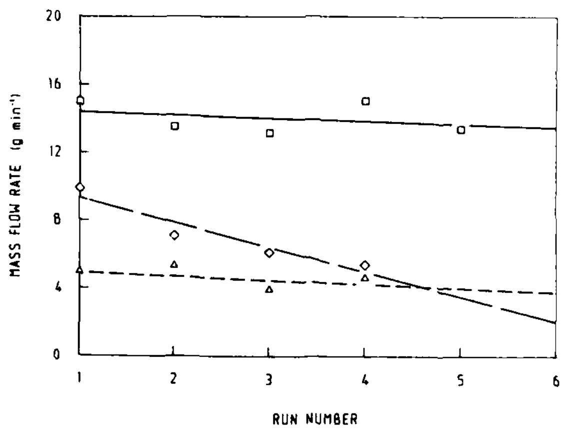


Figure 9 **Change in mass flow rate with repeated testing for B/Pb_3O_4 (10:90) granulated through a BSS 18 sieve using selected solvents; △ acetone, ◇ ethanol, □ water.**

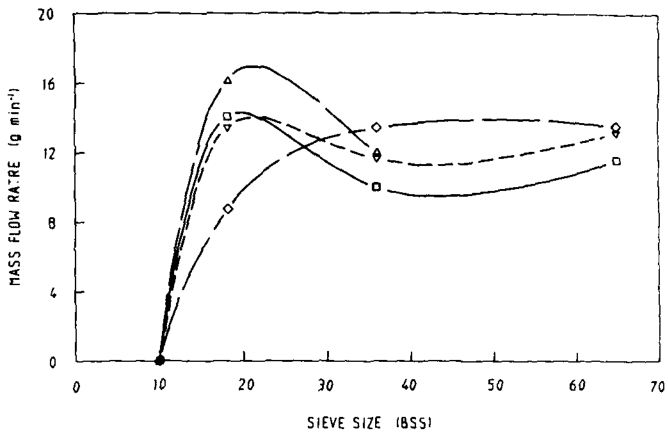


Figure 10 *Change in mass flow rate with sieve size for B/Pb_3O_4 (10:90) granulated with gum arabic binder; ▽ 10% gum arabic solution, △ 5% solution, ◇ 1% solution, □ 0% gum arabic.*

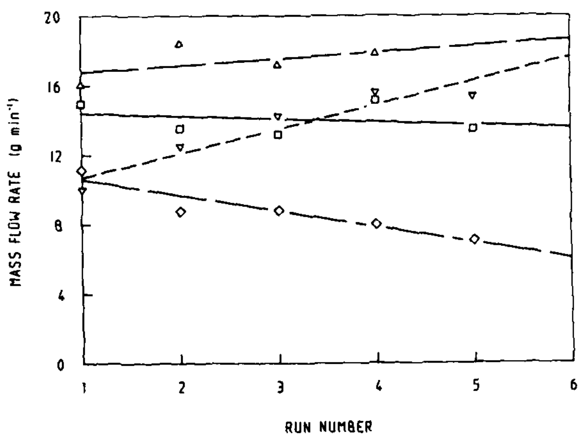


Figure 11 *Change in mass flow rate with repeated testing of B/Pb_3O_4 (10:90) granulated with BSS 18 sieve and selected gum arabic solutions; ▽ 10%, △ 5%, ◇ 1%, □ 0%.*

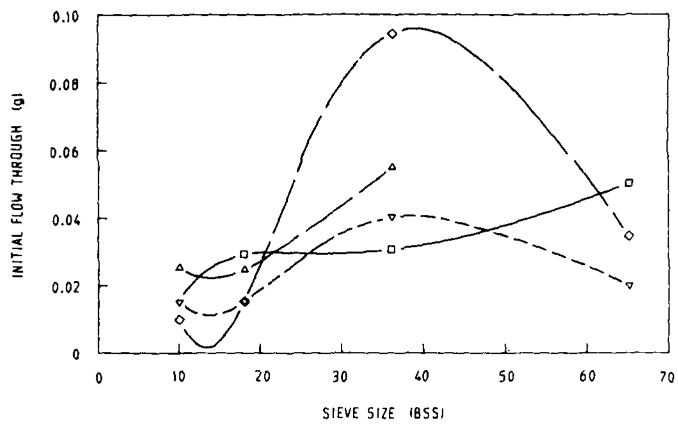


Figure 12 *Initial flow through of B/Pb_3O_4 (10:90) with a range of gum arabic binder solutions for a range of sieve sizes before hopper vibration;* ▽ *10% gum arabic solution,* △ *5%,* ◇ *1%,* □ *0%.*

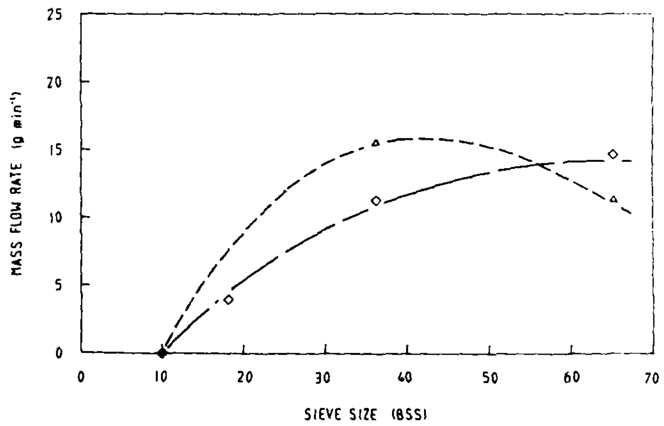


Figure 13 ***Change in mass flow rate with sieve size of B/Pb_3O_4 (10:90) granulated with nitrocellulose lacquer binder;* △ *5% nitrocellulose,* ◇ *1% nitrocellulose.***

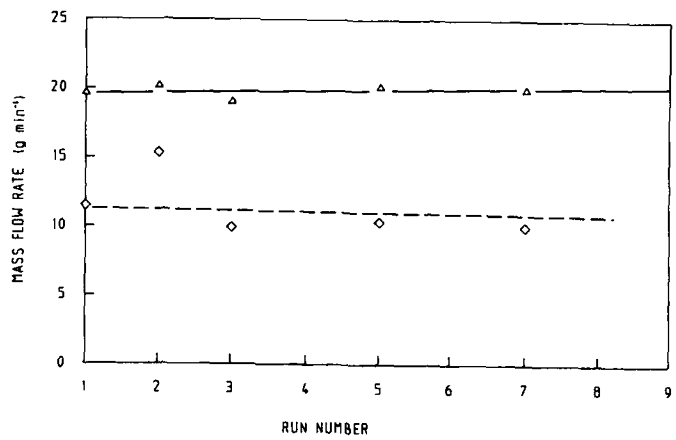


Figure 14 *Change in mass flow rate with repeated testing of B/Pb_3O_4 (10:90) granulated through BSS 36 sieve with nitrocellulose binders;* △ *5% nitrocellulose,* ◇ *1% nitrocellulose.*

SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED

DOCUMENT CONTROL DATA SHEET

REPORT NO.	AR NO.	REPORT SECURITY CLASSIFICATION
MRL-TR-89-32	AR-005-734	Unclassified

TITLE

Methods for improving the flowability of a percussion primer composition

AUTHOR(S)

L.V. de Yong, M. Fitzgerald and B. Whiffen

CORPORATE AUTHOR

DSTO Materials Research Laboratory
PO Box 50
Ascot Vale Victoria 3032

REPORT DATE	TASK NO.	SPONSOR
August 1989	DST 85/170	DSTO
FILE NO.	**REFERENCES**	**PAGES**
G6/4/8-3550	18	37

CLASSIFICATION/LIMITATION REVIEW DATE

CLASSIFICATION/RELEASE AUTHORITY
Chief, Explosives Division MRL

SECONDARY DISTRIBUTION

Approved for public release

ANNOUNCEMENT

Announcement of this report is unlimited

KEYWORDS

Flowability	Granulation	Primer compositions
Flow modifiers	Binders	Primers (explosive)

SUBJECT GROUPS 0079A

ABSTRACT

A vibrating hopper was used to evaluate and determine methods for improvement of the flowability of the percussion primer composition MRL(X) 408. The flowability was enhanced by granulation using both water and binder systems and using flow modifiers (silicon dioxide). Addition of binders reduced the sensitivity of the composition and, when filled into primers, increased the value of peak pressure and the rise time to peak pressure.

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED